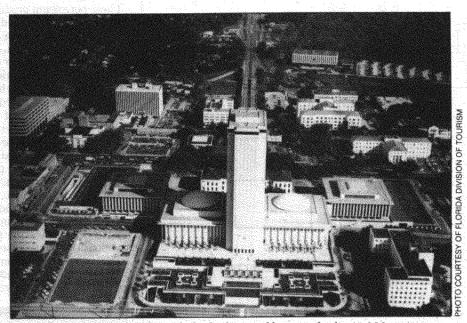
Water Contamination Caused by Gasoline Permeating a Polybutylene Pipe

William G. Leseman



Tallahassee, Fla., the state's capital, obtains potable water for its 45 000 customers from wells that tap the Floridan Aquifer.

A water quality complaint received by the city of Tallahasse, Fla., resulted in an investigation that found contamination of a service line caused by gasoline leaking into the soil surrounding the pipe. The service connection to an apartment was the only incidence of the contamination, but levels of 1,2-dibromoethane were found in one apartment to be 50 times the limit set by the Florida Department of Environmental Regulations. The service line was replaced with copper pipe, which solved the problem.

In September 1984, the city of Tallahasse, Fla., water quality laboratory received a complaint from a customer who said that her water tasted and smelled like paint thinner. Investigation of this complaint found that the water was contaminated by gasoline components, specifically 1,2-dibromoethane (EDB), that had selectively permeated the polybutylene service lines. The lines were buried beneath a parking lot and were exposed to soil contamination caused by leaded gasoline that apparently had leaked from an automobile gas tank. Average ethylene dibromide levels in nine water samples collected from the site were 50 times the maximum contaminant level (MCL) of 0.02 µg/L set by the Florida Department of Environmental Regulations (FDER).

Polyethylene (PE) and polybutylene (PB) pipe have been used to transport potable water for more than 25 years. It

is estimated that there are some 6 million PE and PB service lines in use in potable water systems throughout North America. These plastic pipes have a long

life, are competitive in cost, are flexible and easy to install, and are not corroded by aggressive waters or soils. The Tallahassee Department of Underground Utilities began replacing existing copper and galvanized service lines and routinely installing ¾-in. (20-mm) PB lines in 1968. The utility has now installed approximately 114 mi (183 km) of PB pipe throughout the water service area.

Although plastic pipe is considered

TABLE 1
Major hydrocarbon components of regular gasoline³

Component	Percent by Weight	Boiling Point		
Isopentane	7.88	27.85		
n-Pentane	7.27	36.07		
Toluene	5.92	110.63		
Xylenes (ortho, meta, and para)	7.46	140.00 (average)		
2-Methylpentane	3.85	60.27		
n-Hexane	3.50	68.74		
Ethyl benzene	2.70	136.19		
1,2,4-Trimethylbenzene	2.83	169.35		
3-Methyl-3-ethyl benzene	1.84	161.31		
Benzene	1.35	80.10		
2-Methylhexane	1.25	91.85		

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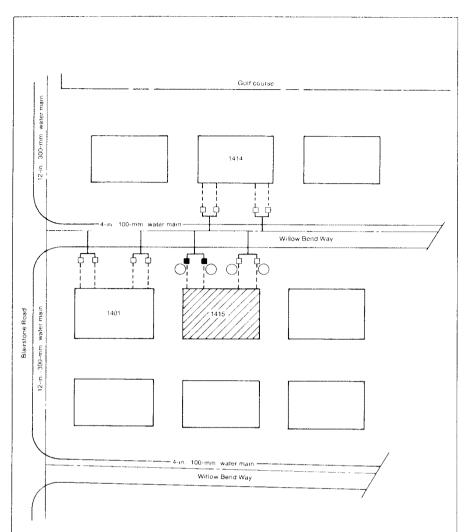


Figure 1. Location of the affected service connection

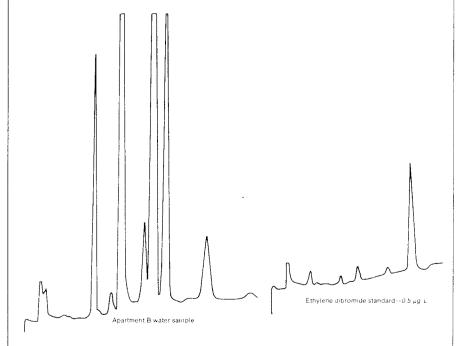


Figure 2. Chromatogram of sample from 1415 Willow Bend Way, apartment B

resistant to chemical attack, manufacturers of plastic pipe warn of possible water contamination through contact with soil that is contaminated by organic solvents. Installation literature recommends that the pipe not be installed in areas where the soil is subject to contamination.

Prediction of soil contamination in an urban environment is difficult. The state of Florida has documented 231 cases of groundwater contamination caused by petroleum products leaking from pipes or storage tanks or by unknown causes.1 These petroleum product leaks will also contaminate surrounding soil. In 1979 Peoples Water Service, a private utility company in Pensacola, Fla., investigated a complaint of an odor of gasoline in the water. The investigation indicated that the soil surrounding the PE service line had been contaminated with about 10 to 15 gal (38 to 57 L) of gasoline leaking from a car parked over the service pipe. Odor analysis was performed and the problem was corrected by removing the soil and replacing the pipe.2

All petroleum products, such as leaded and unleaded gasoline, diesel fuel, kerosene, and other oils and fuels, can potentially cause contamination of potable water by permeating plastic pipe. The composition of such contaminating products consists of a complex mixture of hydrocarbons and additives. Regular gasoline contains more than 180 hydro-

Discussion

Robert P. Walker

Organic solvent contamination of the soils in North America is not commonplace or widespread.1 The Tallahassee incident represents a singular occurrence out of 600 000 ft (180 000 m) of polybutylene pipe used by that city routinely since 1968. It is important to keep such a perspective in focus when addressing the problem of potable water contamination from organic solvents. Based on the documented incidents of permeation of pipe and the estimated 6 million polyethylene (PE) and polybutylene (PB) service connections in use in North America, the odds of contamination from permeation of organic solvents are less than 1 in 100 000. Furthermore, the human taste threshold and odor sensitivity to most common organic solvents have provided sufficient early warning of contamination to prevent any serious long-term illnesses.

TABLE 2
Characteristic components of five petroleum fuels⁴

Component	Regular Gasoline (Six Samples) percent by weight	Unleaded Gasoline (Three Samples) percent by weight	Aviation Gasoline (One Sample) percent by weight	Kerosene (Three Samples) percent by weight	Diesel No. 2 (Three Samples) percent by weight
Benzene	0.47-3.6	<0.2-3.2	<0.2	<0.2	<0.2
Toluene	3.4-10	4.4-12	17	0.23-0.44	< 0.2
Ethyl benzene	1.5-3.1	1.8-4.7	0.77	0.36-0.38	< 0.2
Xvlenes	5.4-11	7.4-16	1.6	0.62-1.3	< 0.2
n-Propyl benzene	0.64-1.0	0.87-1.0	< 0.2	0.25-0.35	< 0.2
1,3,5-trimethylbenzene	1.1-1.6	1.3-3.9	< 0.2	0.51-1.0	< 0.2
Naphthalene	0.1-0.6	0.2-0.5	0.006	0.3-0.6	0.14-0.17
Fluorene	< 0.0003 - 0.02	<0.0003-0.007	0.0005	0.006-0.03	0.07-0.10
Phenanthrene	< 0.0003 - 0.06	<0.0003-0.004	0.0004	0.02-0.03	0.26-0.30
Anthracene	< 0.0001	<0.0001-0.0006	0.00002	< 0.0001	0.013-0.017
Ethylene dibromide	0.015-0.02		0.054		
Lead	0.03-0.43	and the same of th	0.056		

carbons; the most abundant are shown in Table 1 along with their boiling points.³ When gasoline is exposed to the environment, as in a surface spill, the lower boiling point constituents evaporate, and the higher boiling point fraction will be concentrated proportionately.

The determination that contamination comes from petroleum fuel, whether in water or soil, requires the analysis of specific chemical components of the suspected fuel and their relative concentrations. Table 2 shows the characteristic components for five petroleum fuels: regular gasoline, unleaded gasoline, avia-

tion gasoline, kerosene, and No. 2 diesel fuel, along with the range of typical percent of composition by weight. For example, benzene, toluene, and other alkyl benzenes are identified and quantitated to specify gasoline contamination.⁴

To further specify the type of fuel involved in an episode of contamination, EDB is analyzed and quantitated because EDB is added to leaded gasoline and aviation gasoline as a lead scavenger during the fuel blending. It is not found in unleaded gasoline or heavier fuels, such as kerosene and diesel.

If capillary gas chromatography-mass

spectrometry (GC-MS) is available, comparison of GC peak retention time with a fuel standard and MS confirmation of the eluted compound can also be used to determine the type of fuel involved.⁵

Service area description

To understand the evaluation of this water quality complaint, one must understand the nature of the Tallahassee water system. Tallahassee is the state capital and has a minimum of industry. The local economy is based on state government and three universities. The city owns and operates the water utility

Leseman's conclusions are valid and his article is an important contribution to proper water utility management. It should also be pointed out that permeation of organic solvents is not restricted to PE and PB pipes. Virtually all elastomeric and thermoplastic materials have some degree of vulnerability to permeation by certain low-molecular-weight organics.

Contamination via permeation is most often associated with PE and PB service pipes because of their greater likelihood, albeit small, of exposure to organic solvents and their susceptibility to permeation. However, any pipe that utilizes elastomeric gaskets for jointing purposes is also vulnerable to organic solvent permeation. A recent study assessed the permeation of gasket materials and compared permeation through gasketed and nongasketed pipes.² Permeation has

always been greater for gasketed pipes. Some elastomers are more resistant to permeation than others because of their composition and density. Specialty gaskets formulated to limit permeation are expensive, but worst of all, they provide an inferior compression seal for joining buried pipes. Their increased density significantly compromises their elasticity. Furthermore, such gaskets are not permeation proof.

Can permeation be prevented? It is not realistic to believe that permeation can be totally eliminated since virtually all water pipes rely on elastomeric gasket joints. The likelihood of permeation can, however, be reduced through stricter requirements for liquid storage tanks. Perhaps even more important is a program to increase public awareness of the dangers associated with improper disposal of organic solvents. The trite

expression, "An ounce of prevention is worth a pound of cure," is prudently applicable.

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TABLE 3							
Average concentration of ethylene dibromide in apartments at 1415 Willow Bend Way							

	Be	After Service Change		
Apartment	Inside Faucet	Outside Faucet	At Meter	Outside Faucet
A	*	*	*	*
В	1.69	1.37	0.79	*
С	*	*	*	*
D (vacant)		0.89	0.79	*

^{*}Below detection limit of 0.005 µg/L

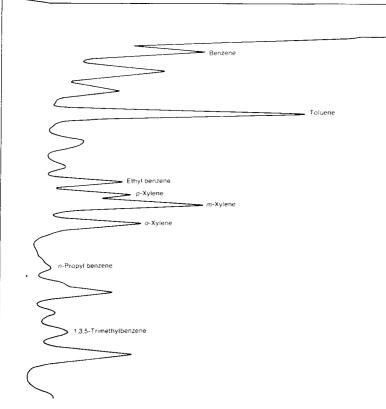


Figure 3. Aromatic hydrocarbon analysis of contaminated soil

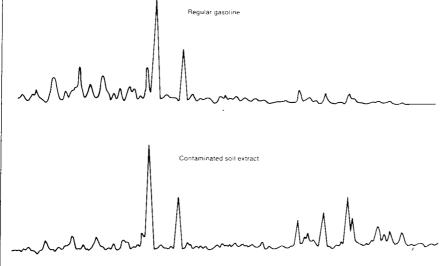


Figure 4. Chromatogram of regular gasoline and acetone extract of contaminated soil

as part of the Department of Underground Utilities, which includes gas, water, and wastewater. All water quality complaints are directed to the water quality laboratory, which is a division of underground utilities. Potable water is obtained from 20 deep wells with an average depth of 350 ft (107 m), which are drilled into the Floridan Aquifer. The wells are located throughout the service area and range in diameter from 8 to 16 in. (20 to 40 cm). All wells are analyzed twice a year for primary and secondary standards for volatile organics and synthetic organic chemicals. Average pumping for the system is 19 mgd (72 ML/d), which serves 45 000 customers. No treatment is required to meet state primary and secondary standards. Chlorine is injected at each well to maintain a residual of 0.2 mg/L at the far end of the distribution system according to FDER rules. Average raw water analyses over the past two years have shown no synthetic organic compounds. Total trihalomethanes (THMs) average $<4 \mu g/L$.

Complaint description

The complaint about the taste and odor of tap water was received Sept. 18, 1984. The customer lived in an apartment complex consisting of separate units with four apartments per unit. The building was less than five years old and was located adjacent to a public golf course in a highly developed middle-class area (Figure 1).

A water well operator trained in sampling techniques was dispatched to the apartment to evaluate the complaint. He noted that the water did indeed smell like paint thinner and that the odor was persistent. A 40-mL sample from 1415 Willow Bend Way, apartment B, the location of the complaint, was collected using a vial lined with PTFE septa. The sample was analyzed using a purge-and-trap concentration with GC analysis. External standards were used for qualitative as well as quantitative confirmation.

The purge-and-trap gas chromatograph-electron capture detector (GC-ECD) method was developed by the water quality laboratory to quantify the very low levels ($<4 \mu g/L$) of THMs in the water supply and has also proved satisfactory for detection and quantification of low levels of chlorinated organics in drinking water. The method is essentially the same as US Environmental Protection Agency Method 601, but the use of the ECD detector provides lower detection limits for some of the halogenated compounds. Special care must be taken when using this method. All gases must be ultrapure, carrier grade and cleaned further by the use of 5-A molecular sieve traps.

Surprisingly, the initial sample showed the presence of EDB at a concentration

of 1.02 μ g/L, 50 times the FDER limit of $0.02 \,\mu g/\bar{L}$. This finding was unexpected and somewhat discounted; however, the presence of EDB was confirmed by using a second column and comparing retention times to an external standard. A second sample was collected to eliminate the possibility of contamination of the sample bottle, and it showed a concentration of 0.85 µg EDB/L (Figure 2). The customer, who had been using bottled water since first noticing the odor, was contacted and instructed not to drink the water while a sampling survey was conducted on the distribution system in the immediate area. Four samples were collected from within 0.5 mi (0.8 km) of the location of the complaint. All four samples were negative for EDB contamination. This survey eliminated the possibility of widespread contamination of the distribution system.

Maintenance records for the distribution system in the complaint area were reviewed, and nothing unusual was noted. The service connection for the apartments at 1415 Willow Bend Way had had a leak in June 1983, which had been repaired. It was also noted in the records that the 3/4-in. (20-mm) service connections in that area were constructed of PB pipe. No leaks for this service connection had been reported in previous years, and interviews with the apartment management concluded that no internal problems had occurred.

Additional analytical work now focused on the apartment building and the two PB service connections that delivered water to the four apartments. Samples were collected from each apartment at the meter by disconnecting the meter from the service. The results shown in Table 3 indicated that the contamination was limited to one service connection serving two apartments. Apartments A and C were not affected, and apartment D was vacant.

Next it became necessary to determine where and how EDB had entered this particular water service connection. There were three theories that were advanced by laboratory and water production personnel: (1) contact between the PB service pipe and an EDB-containing organic solvent that was present in the soil; (2) contamination through backflow; and (3) soil contamination through disposal or application of EDB at the adjacent golf course prior to installation of the water service.

Determination of the cause of contamination

Because samples had been collected from adjacent apartment units and the results of analysis showed less than detectable levels, the possibility that the contamination was caused by a cross connection or backflow was eliminated.

The service line delivering the con-

taminated water was excavated, and it was observed that the asphalt pavement at the edge of the sidewalk, approximately 5 to 7 ft (1.5 to 2.1 m) from the meter, was soft, crumbly, and had lost its binding ability. The soil beneath this area and surrounding the PB service line had a strong odor of a solvent or gasoline. Soil samples were collected to determine the source of the odor. The service line was replaced with copper pipe, and samples were collected from the apartments in the unit. All samples analyzed for EDB were below detectable levels, which confirmed that the contaminant had permeated the PB service line.

The location of contaminated soil under a parking lot, along with the physical properties of the pavement overlying the soil, provided evidence that the contamination was probably caused by gasoline spilled on the surface. In order to confirm this theory, the soil was analyzed for aromatic and alkyl aromatic hydrocarbons and EDB, and an acetone extract of the soil was analyzed using capillary GC-MS.

Alkyl aromatic hydrocarbons were analyzed using purge and trap with GC-flame ionization detection (FID). External standards were used for qualitative analysis. Figure 3 shows the packed column chromatogram of the soil. The presence of benzene, toluene, ethyl benzene, and xylenes provided evidence of a fuel spill.

The same EDB analytical procedure used for water was used for soil. Two and a half grams of soil were introduced into the purge-and-trap sample vessel and purged in the same manner as in the previous procedure. Only the EDB peak was identified and confirmed.

A GC with a capillary column interfaced with an MS was used to analyze acetone extracts of the contaminated soil. Retention times and mass spectrum peaks observed in the soil extract were compared with peaks obtained from a sample of regular gasoline, thus confirming that the soil was contaminated with leaded gasoline. Determining the individual compounds in the gasoline by comparison with known standards was not required, and the method provided adequate proof that the source of contamination was regular gasoline. Figure 4 shows a comparison of peak retention times in the range of 14-18 min for regular gasoline and the soil sample with mass spectrum of the peaks plotted for each peak.

Conclusion

It is necessary to recognize the danger signs of permeation of organics through plastic pipe.

Utilities should maintain records of the date and type of water mains and service connections installed. If customers complain of an odor or taste of organic solvents in their water where PE or PB pipe has been installed, a thorough check of the ground surface is recommended. Areas of dead grass, old or junk automobiles, or disintegrating pavement are good indications of possible contamination.

Even if the water utility has not installed PB or PE service connections, customers or plumbers often install PB pipe from the meter to the residence; consequently, the utility will not have a record of such an installation.

The solution to such a problem is the immediate replacement of the contaminated pipe and removal and replacement of the contaminated soil. The customer's lines should be flushed and samples collected to ensure that there is no residual organic contamination left in the lines.

Acknowledgment

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